

TECHNICAL REPORT 1970  
September 2008

# **Rapid Sediment Characterization Tools**

V. J. Kirtay

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distribution is unlimited.

SSC San Diego



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This report was prepared for the Naval Facilities Engineering Service Center (NFESC) Ecological Risk Technical Assistance Team (ERTAT) by the Environmental Sciences Branch (Code 71750) of the Advanced and Applied Sciences Division (Code 717), SPAWAR Systems Center San Diego (SSC San Diego).

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## EXECUTIVE SUMMARY

The initial goals of most environmental site characterization and restoration programs are to identify potential contaminant sources and to delineate areas of contamination. However, traditional sampling and analysis approaches do not always provide all the information necessary to support these processes in an efficient and cost-effective manner. Site assessments performed in the marine environment are often hindered because of the complexity and heterogeneity of marine ecosystems. Therefore, the implementation of additional measures to facilitate the site assessment and remediation process is specifically dictated for U.S. Navy sites by policy. One of the measures that can be implemented at various stages of these processes at sediment sites is the use of rapid sediment characterization (RSC) technologies. These technologies are, in most cases, field-based analytical tools that measure chemical, biological, or physical parameters on a real-time or near real-time basis. When used appropriately, these tools can streamline many aspects of field investigations. The tools can be used to delineate areas of concern, fill in information gaps, and ensure that expensive, certified analyses have the greatest possible impact.

This guide provides information about several of the rapid sediment characterization technologies that can be used at marine sediment sites, including common techniques such as X-ray fluorescence for metals, immunoassays for polycyclic aromatic hydrocarbons and polychlorinated biphenyls, QwikSed bioassay for assessing toxicity, and other more specialized techniques. Examples are provided to illustrate the efficacy of applying rapid sediment characterization tools for a broad range of applications, including remedial investigations/feasibility studies, total maximum daily load studies, and forensic studies. Finally, recommendations are given for the evaluation, selection, and application of RSC tools within these processes.



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## ACRONYMS

BERA	Baseline Ecological Risk Assessment
BRAC	Base Realignment and Closure
COPEC	Contaminant of Potential Ecological Concern
Cu	Copper
DBMS	Database Management System
DMA	Demonstration of Method Applicability
DQO	Data Quality Objective
ELISA	Enzyme-linked Immunosorbent Assay
EIA	Enzyme Immunoassay
ERA	Ecological Risk Assessment
EDXRF	Energy Dispersive X-ray Florescence Spectrometry
FIA	Fluorescent Immunoassay
FPXRF	Field-Portable X-ray Fluorescence Spectrometry
FRTR	Federal Remediation Technologies Roundtable
FS	Feasibility Study
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GIS	Geographic Information System
GPS	Global Positioning System
HPAH	High Molecular Weight PAHs
HPS	Hunters Point Shipyard
IA	Immunoassay
ICP/AES	Inductively Coupled Plasma/Atomic Emission Spectrometry
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ITRC	Interstate Technology Regulatory Council
Li	Lithium
LPAH	Low Molecular Weight PAHs
LEDO	Long-term Effects of Dredging Operations
LISST	Laser In Situ Scattering and Transmissometry
mg/kg	milligram per kilogram
MVS	Metals Verification Study
NPL	National Priorities List
PAH	Polycyclic Aromatic Hydrocarbon
Pb	Lead
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PRGs	Preliminary Remediation Goals
PSNS	Puget Sound Naval Shipyard
QA/QC	Quality Assurance/Quality Control
RGS	Reporter Gene System
RIA	Radioimmunoassay
RI/FS	Remedial Investigation/Feasibility Study
RPM	Remedial Project Manager
RSC	Rapid Sediment Characterization

Si	Silicon
SSC San Diego	SPAWAR Systems Center San Diego
SQS	Sediment Quality Standards
SRA	Screening Risk Assessment
TIP	Technology Innovation Program
TMDL	Total Maximum Daily Load
μ	micron
μg/kg	microgram per kilogram
USEPA	United States Environmental Protection Agency
UVF	Ultra Violet Fluorescence Spectroscopy
XRF	X-ray Fluorescence Spectrometry
Zn	Zinc

## INTRODUCTION

This report is an update to an issue paper, *Rapid Sediment Characterization (RSC) Tools for Ecological Risk Assessment* [1], published to support Remedial Project Managers (RPMs) conducting ecological risk assessments at U.S. Navy sediment sites. Since its publication, advances on several fronts have led to wider acceptance of the role that real-time and near real-time measurement technologies (often referred to as screening tools, field-based measurement technologies, or rapid characterization technologies) play in improving the cost-effectiveness and efficiency of contaminated site restoration activities, total maximum daily load (TMDL) assessments, and contaminant fingerprinting/source identification (forensics) studies.

The traditional approach to site characterization and cleanup is based on a multi-stage (and often iterative) process where site decisions are made after all the data have been collected and evaluated. This approach entails numerous field sampling events to complete the project in the required stages. Iterations to the project are guided by off-site evaluations that add to the length and cost of the project. While members of the environmental community recognize that this approach can significantly increase the duration and expense of cleanup projects, the ability to diverge from this approach is challenging because many programs require multiple stages, and contaminant distribution and geological heterogeneity, particularly in the marine environment, are complex and require large numbers of samples to reduce uncertainty so decisions can be made.

While not considered a mandatory element to site assessment, cleanup, monitoring, etc., field analytical technologies are gaining acceptance in these programs as witnessed by the growing number of contaminated sites where they are used to support the decision-making process and by the numerous websites and documents (see [Additional Resources](#) section) dedicated to their application. Within the Department of the Navy, two different policies, *Navy Policy for Conducting Ecological Assessments* [2], and *Navy IR Sediment Policy* [3], have long invoked the use of advanced chemical and biological screening technologies to support sampling sediment chemistry and other sampling programs whose focus is primarily on identifying the potential sources of contamination and delineating the areas of contaminated media. Continued improvements (e.g., smaller, faster, more rugged) in the technologies over the past decade, significant progress in telecommunications and computer software, and changes to the overall approach to Environmental Project Management [4] have all been factors in the increasing role field analytical technologies have in generating “effective” data to support making defensible project decisions.

This report updates the advances made in field analytical technologies, addresses current thinking on the application and effective use of field-generated data, and highlights, via case studies, the expanded roles RSC tools are filling at Navy and non-Navy sediment sites.

## RSC: WHAT IS IT?

Over a decade ago, the nature and extent of contamination at sediment sites was not being adequately delineated, which led to longer and more costly site assessments. This situation was largely caused by the complexity and heterogeneity of marine ecosystems and the challenges posed by sampling and subsequent analysis of the marine sediments. Therefore, several analytical technologies or methods were developed or modified to provide measurements of chemical, physical, or biological parameters in marine sediments on a real-time (instantaneous) or near real-time (requires some sample treatment) basis in the field or laboratory to more adequately characterize the extent of contamination while reducing the number of field deployments. Thus, the term, Rapid Sediment Characterization (RSC) (see Box 1), was coined to differentiate between a broad suite of field analytical tools that were used to provide rapid results for a

wide range of analytes in soil, water, and air versus a smaller suite of tools that could make rapid measurements in marine sediments. While the definition is still relevant, advances in computer software and wireless technologies have allowed the definition to expand to include technologies that support data management, processing, interpretation, and sharing.

#### **Box 1. Rapid Sediment Characterization (RSC)**

- *Rapid sediment characterization* can be defined as the utilization of real-time or near real-time screening techniques to rapidly delineate the extent of contamination, physical characteristics, and/or biological effects in sediment.
- *Rapid sediment characterization tools* are analytical tools that provide measurements of chemical, physical, or biological parameters on a real-time or near real-time basis and are used in a field or laboratory setting for sediment.
- *Rapid sediment characterization data management tools* are tools used to manage, process, interpret, and share data.

Several organizations provide information, accessible via the Internet, on field analytical technologies, test methods, software programs, and guidance. The U.S. Environmental Protection Agency (USEPA), through its Technology Innovation Program (TIP), has compiled an online compendium of field analytic technologies that provides information about technologies that can be used in the field to characterize contaminated soil, sediment, groundwater, and air, and to monitor the progress of remedial efforts and, in some cases, confirm sampling and analysis for site close-out. Additionally, the USEPA has developed SW-846 standard methods (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) for several field screening tools such as X-ray fluorescence (XRF) spectrometry and immunoassays. The Federal Remediation Technologies Roundtable (FRTR) is a collaborative effort among federal agencies to promote interagency cooperation to advance the use of innovative technologies to clean up hazardous waste contamination. They have developed online tools to assist users in evaluating and selecting time- and cost-effective innovative technologies to characterize and clean up hazardous waste sites. The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition working together with industry and stakeholders to achieve regulatory acceptance of environmental technologies. The Triad Resource Center, which is a federal/state interagency partnership, provides the information hazardous waste site managers and cleanup practitioners need to implement the Triad approach effectively (see Box 2). The components that are central to this approach reflect the most current thinking in using real-time/near real-time measurement technologies for on-site decision-making, and are supported by the USEPA, FRTR, and ITRC, as well as other organizations.

#### **Box 2. TRIAD**

The Triad approach to decision-making for hazardous waste sites offers a technically defensible methodology for managing decision uncertainty that leverages innovative characterization tools and strategies. The Triad refers to three primary components, **systematic planning, dynamic work strategies, and real-time measurement systems**.

Source: Triad Resource Center. "Triad Overview. <http://www.triadcentral.org/over/index.cfm> (Accessed October 2007)

Most commercially available field analytical tools are used for chemical analysis of soil, gas, and groundwater. A few tools are available for geophysical analyses, while even fewer tools/techniques are commercially available for biological analyses. Although many of the technologies are not applicable to marine sites, many technologies have been tested and successfully demonstrated at marine sediment sites (Table 1). Progress continues in developing “rapid” biological screening assays that work on the cellular level. While they cannot technically be considered field screening tools, they potentially offer a more rapid means of characterizing the extent of contamination at sites and provide information on the toxicological potency of mixtures of contaminants.

Table 1. Examples of rapid sediment characterization tools demonstrated in marine sediments.

Measurement Type	Analytical Technique	Analyte(s)	Analysis Location
Chemical	XRF spectroscopy	Metals (Cu, Zn, Pb)	Field or lab
	Ultraviolet fluorescence (UVF) spectroscopy	PAHs	Field or lab
	Immunoassay	PAHs PCBs Pesticides Dioxins	Field or lab
Physical	Laser particle scattering,	Grain size (% fines)	Field or lab
	Infrared (IR) moisture analyzer	Moisture content (%)	Field or lab
Biological	QwikLite™ bioassay	Organic (PAHs), inorganic (metals)	Mobile field Lab or lab
	*Biomarkers (P450RGS dioxin screening assay)	Dioxins, PAHs	Lab
	*cDNA microarrays	Dioxins, PAHs, PCBs	Lab

\*These assays are considered “rapid” (e.g., 1 to 2 weeks) compared to standard methods (1 to 2 months), but they are not classified as real-time/near real-time techniques.

Managing, analyzing, visualizing, and sharing large data sets has changed dramatically over the past decade. Several free and proprietary software packages are available to improve data effectiveness. Table 2 provides a condensed list of tools frequently used to support environmental data management and decision-making. The USEPA also provides information and access to a wide variety of decision support tools (<http://www.frtr.gov/decisionsupport/>) that are freely available to the public. These tools are well-suited for applications that utilize field analytical tools [5].

Selecting any analytical platform, including those in Table 1, should be made only after careful systematic planning has considered the pros and cons of each option in the context of project decision goals (Data Quality Objective [DQO] process), contaminants of concern, site logistics, budget, etc. [6]. The following questions should be addressed before selecting and applying any technology:

- What are the goals of the investigation?
- What are the contaminants of concern?
- Are the contaminants known?
- What are the action limits?
- What are the strengths and weaknesses of the analytical methods being considered?
- Do instrument detection limits meet action limit requirements?

Addressing these and other questions within the framework of the overall decision-making process will ensure that more defensible, cost-effective, and innovation-friendly approaches to environmental decision-making are made.

Table 2. Frequently used data management and decision support tools.

Data Management and Decision Support Tools	Description	Examples	Additional Information/Sources <sup>1</sup>
Global Positioning System (GPS)	A system of satellites, computers, and receivers that determines the latitude and longitude of a receiver on Earth by calculating the time difference for signals from different satellites to reach the receiver.	<ul style="list-style-type: none"> <li>Trimble® GPS and GIS Systems for Natural Resources</li> <li>Garmin® GPS Systems</li> </ul>	<ul style="list-style-type: none"> <li><a href="http://www.trimble.com/index.aspx">http://www.trimble.com/index.aspx</a></li> <li><a href="http://www.garmin.com/garmin/cms/site/us">http://www.garmin.com/garmin/cms/site/us</a></li> </ul>
Database Management System (DBMS)	A DBMS is a complex set of software programs that controls the organization, storage, management, and retrieval of data in a database.	<ul style="list-style-type: none"> <li>Microsoft Access</li> <li>Oracle®</li> <li>Microsoft SQL Server®</li> <li>MySQL®</li> </ul>	<ul style="list-style-type: none"> <li><a href="http://en.wikipedia.org/wiki/MS_Access">http://en.wikipedia.org/wiki/MS_Access</a></li> <li><a href="http://en.wikipedia.org/wiki/Oracle_Database">http://en.wikipedia.org/wiki/Oracle_Database</a></li> <li><a href="http://en.wikipedia.org/wiki/Microsoft_SQL_Server">http://en.wikipedia.org/wiki/Microsoft_SQL_Server</a></li> <li><a href="http://en.wikipedia.org/wiki/MySQL">http://en.wikipedia.org/wiki/MySQL</a></li> </ul>
Geographic Information Systems (GIS)	GIS is a tool that allows users to create interactive queries (user-created searches), analyze the spatial information, edit data, maps, and present the results of all these operations.	<ul style="list-style-type: none"> <li>ESRI® GIS and Mapping Software (ArcGIS®)</li> <li>BASINS v.4.0</li> <li>INDRISI® Andes GIS and Image Processing Software</li> </ul>	<ul style="list-style-type: none"> <li><a href="http://www.esri.com/index.html">http://www.esri.com/index.html</a></li> <li><a href="http://www.epa.gov/waterscience/ftp/basins/system/BASINS4/">http://www.epa.gov/waterscience/ftp/basins/system/BASINS4/</a></li> <li><a href="http://www.clarklabs.org/">http://www.clarklabs.org/</a></li> </ul>
Statistical/Geostatistical Analysis	Geostatistics offers a way of describing the spatial continuity of natural phenomena and provides adaptations of classical regression techniques to take advantage of this continuity [7].	<ul style="list-style-type: none"> <li>SAS® Statistical Analysis</li> <li>ProUCL 4.0 for Environmental Applications</li> <li>ArcGIS® Geostatistical Analyst</li> <li>Stanford Geostatistical Modeling Software (S-GeMS)</li> </ul>	<ul style="list-style-type: none"> <li><a href="http://www.sas.com/technologies/analytics/statistics/stat/cs/stat/">http://www.sas.com/technologies/analytics/statistics/stat/cs/stat/</a></li> <li><a href="http://www.epa.gov/esd/tsc/software.htm">http://www.epa.gov/esd/tsc/software.htm</a></li> <li><a href="http://www.esri.com/software/arcgis/extensions/geostatistical/index.html">http://www.esri.com/software/arcgis/extensions/geostatistical/index.html</a></li> <li><a href="http://pangea.stanford.edu/~nremy/GEMS/">http://pangea.stanford.edu/~nremy/GEMS/</a></li> </ul>
Mapping Applications	2-D and 3-D geospatial analysis and visualization platforms.	<ul style="list-style-type: none"> <li>Surfer®</li> <li>ArcView®</li> <li>Earth Vision®</li> </ul>	<ul style="list-style-type: none"> <li><a href="http://www.ssg-surfer.com/">http://www.ssg-surfer.com/</a></li> <li><a href="http://www.esri.com/software/arcview/">http://www.esri.com/software/arcview/</a></li> <li><a href="http://www.dgi.com/earthvision/index.shtml">http://www.dgi.com/earthvision/index.shtml</a></li> </ul>

<sup>1</sup> Inclusion of any resource in this listing does not constitute an endorsement by the U.S. Navy.

## RSC TOOLS: HOW DO THEY WORK?

Understanding how rapid sediment characterization tools or any analytical tool for that matter work and how they can support the decision-making process requires more than a general knowledge of the tool itself. It requires understanding the general distinction between standard analytical methods and field methods (e.g., RSC Tools), and perhaps more importantly, understanding what type(s) of data they can produce, and how the data can be used to best support the decision-making process.

Standard laboratory methods (also referred to as definitive methods) and rapid characterization methods (also referred to as screening methods) are typically characterized by certain strengths and weaknesses (Table 3). In general, rapid characterization methods are less expensive and provide higher data density more quickly than standard laboratory methods. The lab methods, while typically more expensive and time-consuming, have the advantage of producing data of higher analytical certainty (lower detection limits, more quantitative) and can provide much more analytical specificity (e.g., specific PCB congeners as opposed to a class of Aroclors<sup>®</sup>).

Table 3. Strengths and weaknesses of screening and standard laboratory methods.

Rapid Sediment Characterization Analysis	Standard Laboratory Analysis
Strengths	Strengths
High spatial/data density	Low detection limits
Reduced cost per sample	Analyte specificity
Rapid results can guide further sampling	More quantitative
Weaknesses	Weaknesses
Often non-specific	Higher cost per sample
Often more sensitive to sample matrix	Longer turn-around time
Typically less quantitative	Difficult/expensive to characterize heterogeneous contamination (blind sampling)

While this type of classification—standard methods versus field methods—is essentially correct and is accepted by the environmental community, when it comes time to selecting analytical methods to support a project, environmental decision-makers and practitioners still frequently assume that definitive analytical methods generate definitive data (high data quality, legally defensible) while screening methods generate screening data (poor data quality, useful information but of limited use in supporting project decisions), and therefore tend to opt for the standard laboratory methods. This assumption is incorrect. Data produced by screening methods can be of known and documented quality and adequate quality control can be used in conjunction with data generated in the field.

As thoroughly discussed in the paper, “Applying the Concept of Effective Data to Environmental Analyses for Contaminated Sites” [6], screening methods tend to have more uncertainty in analyte identification and quantification than methods that are considered definitive, definitive methods themselves are far from foolproof. Even methods such as inductively coupled plasma/atomic emission spectrometry (ICP/AES) and gas chromatography/mass spectrometry (GC/MS) are not free from interferences that can compromise data quality. When data quality issues are treated as if they were solely dependent on method requirements and independent of data use, a singular focus on managing analytical error can trigger major decision errors. Environmental decisions are especially susceptible to error in site cleanup situations because the major source of decision uncertainty (as much as 90% or more by some estimates) is caused by sampling variability as a direct consequence of the heterogeneity of environmental matrices [6].

Ironically, highly accurate data points of documented quality from standard methods may form a poor quality data set that produces misleading conclusions and erroneous project decisions. Typically, analyzing samples using a highly accurate method is very expensive; therefore, the number of samples used to determine the presence and degree of contamination is limited. Even if the data points themselves are perfect, an inaccurate assessment is likely when a few samples cannot accurately locate or represent site contamination (i.e., the samples are not representative of the site in the context of the intended decisions about the site). A much more accurate picture of the site is gained when many samples are analyzed, even if the analytical method itself is somewhat less accurate [6].

The key to defensible environmental decision-making is to openly acknowledge all underlying assumptions and to manage all sources of uncertainty that can significantly impact the accuracy of a decision. Often, a weight of evidence approach is needed because no single piece of information can provide definitive evidence, given the complexities present in environmental systems. A data set that might not be effective for making a certain decision when considered alone may become part of an effective data set when considered in conjunction with other relevant information, such as another data set that contains supporting or complementary information. An example of this is when the cost of a definitive analytical method may prohibit the sampling density needed to manage sampling uncertainty, whereas existing screening analytical methods cannot supply all the analytical quality needed. Intelligent sampling and analysis design may allow for the selection of an inexpensive screening method to manage sampling uncertainties, while prudent confirmatory analysis of selected samples by the definitive method manages for residual analytical uncertainties in the data set produced by the screening method. In this way, the two data sets collaborate to produce data that are effective for supporting the final decision(s) [6].

## **RSC TECHNOLOGIES: GENERAL PRINCIPLES**

The RSC technologies addressed here range from mainstream, widely used technologies such as XRF and immunoassays to more specialized, less-frequently used technologies specifically designed for the aquatic environment (e.g., Laser In Situ Scattering and Transmissometry [LISST], QwikSed) to fairly complex biological tools that can be used to support analyte detection in sediments as well as assess the impact of environmental stressors on the aquatic environment (e.g., biomarkers).

As is the case with any technology, recognizing its limitations (e.g., interferences, sensitivity, accuracy, etc.) before use is critical to its successful implementation. A brief summary of the RSC tools is provided below. Additional references and links to other resources for these tools are provided at the end of this report.



## **CHEMICAL TOOLS**

### **XRF for Metals**

XRF is a nondestructive method for the elemental analysis of solids and liquids. The sample is irradiated by an intense x-ray beam, which causes the emission of fluorescent x-rays. The emitted x-rays can be detected using energy dispersive or wavelength dispersive detectors. The energies or wavelengths of the emitted x-rays are used to identify the elements present in the sample, while the concentrations (how much) of the elements are determined by the intensity of the x-rays. XRF is a bulk analysis technique, with the depth of sample analyzed varying from less than 1 mm to 1 cm, depending on the energy of the emitted x-ray and the sample composition. The elements commonly detected range from sodium to uranium. Lighter elements from boron to fluorine may also be detected [1], [8].

XRF spectrometry is the choice of many analysts for elemental analysis. XRF spectrometry easily and quickly identifies and quantifies elements over a wide dynamic concentration range, from part per million levels up to virtually 100% by weight, although detection limits vary for each element. XRF spectrometry does not destroy the sample and requires little, if any, sample preparation. Overall, the analysis turnaround time is very fast. These factors significantly reduce the per sample analytical cost when compared to other elemental analysis techniques. Some of the primary elements of environmental concern that energy dispersive XRF (EDXRF) can identify are arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, silver, and zinc [9].

For the environmental analysis of sediment samples, samples are analyzed *ex situ* (in sample cups) with minimal preparation. After homogenization, samples can be analyzed “wet” or dried, ground, and analyzed. Typical analysis times range from 30 to 200 sec per sample. Increased sample preparation and analysis times can improve accuracy and measurement precision. While XRF can measure a wide range of metals simultaneously, Pb, Zn, and Cu are the most commonly measured elements in marine sediments. Sediment benchmarks for other relevant metals are typically too low to be detected by field-portable XRFs. Detection limits for Pb, Zn, and Cu typically range from 50 to 150 ppm using a field- portable XRF (FPXRF). Lower detection limits can be achieved in the laboratory using more powerful bench-top EDXRF systems (e.g., 20 to 50 ppm) [1]. Several examples in the literature show that XRF has been used in the field and the laboratory to analyze soils and sediments [10], [11]. USEPA has certified FPXRF as a field screening method for metals in soil and sediment (EPA Method 6200 [12]).

### **UVF Spectroscopy for PAHs**

This screening method is based on the measurement of fluorescence observed following UV excitation of organic solvent extracts of sediments. In general, this method measures fluorescent organics (especially PAHs), though care must be taken to reduce signals from natural organic compounds (e.g., humics) that fluoresce. Because fluorescence measurements are matrix-sensitive, measurements must be made on solvent extracts rather than directly on the wet, solid sediment sample to achieve detection limits appropriate for marine sediment PAH benchmark criteria and typical levels in many marine sediments. Solvent extraction requires additional time for sample extract analysis, so although fluorescence is a near real-time measurement, the total analysis time may be up to half an hour. Solvent extraction makes it possible to improve detection limits by several orders of magnitude. Detection limits range from 1- to 5-ppm total solid-phase PAH. Many studies have used UVF to assess total PAH levels in various types of sediment [13]–[15].

## **Immunoassays for PCBs, PAHs, Pesticides, and Dioxins**

Immunoassay is a technology for identifying and quantifying organic and inorganic compounds. Immunoassay uses antibodies that have been developed to bind with a target compound or class of compounds. The technology has been used widely for field analysis in the environmental field because the antibodies can be highly specific to the target compound or group of compounds and because immunoassay kits are relatively quick and simple to use. Concentrations of analytes are identified through the use of a sensitive colorimetric reaction. The target analyte's presence is determined by comparing the color developed by a sample of unknown concentration with the color formed by the standard containing the analyte at a known concentration. Using a photometer or spectrophotometer, the color intensity of the sample can be used to determine the analyte concentration [16].

There are four types of immunoassay: (1) enzyme immunoassay (EIA), (2) radioimmunoassay (RIA), (3) fluorescent immunoassay (FIA), and (4) the enzyme-linked immunosorbent assay (ELISA), which is used most often for environmental field analysis because it can be optimized for speed, sensitivity, and selectivity, and because it contains no radioactive materials. ELISA has a longer shelf life and is simpler to use than other immunoassay methods. RIA and FIA are seldom used for environmental sample analysis [16].

For marine sediments, this technology is most often used to measure concentrations of various organic contaminants, including PCBs, PAHs, organic pesticides, and dioxins. Detection limits for PAHs and PCBs, the more commonly measured constituents in marine sediment, are approximately 0.5 mg/kg for PAHs and range from 0.1 to 0.2 mg/kg for PCBs, depending on the sediment matrix (sand versus silt) and the presence of other contaminants [17], [18]. Detection limits for dioxins are quoted in the part per trillion ranges using a modified USEPA Method 4025 [19]. Individual immunoassay testing products are reviewed and accepted by the EPA Office of Solid Waste for the detection of sample analytes in specified matrices. Various testing products produced by several different developers may be available for the same compound(s) and matrices. Each method was formulated using independently developed reagents that may result in significantly different performance characteristics and limitations [20]. Several test kits are commercially available and range in cost from \$10 to \$40 per sample per kit.

## **PHYSICAL TOOLS**

### **Laser Particle Scattering for Grain Size**

Laser particle scattering operates on the principle of small-angle (Rayleigh) laser scattering to obtain the size distribution of particles suspended in water. The small angle intensity distribution of light scattered by particles suspended in water is recorded. This distribution, which is the sum of particle scattering, is inverted to obtain the particle concentration and size spectrum. Theoretically, the particle size range is 0.1 to 500  $\mu$ . Commercial instruments such as the LISST are available for making in situ measurements (submersible) and measurements of samples in the laboratory, on the manufacturing line, or in a small boat [21]. The operating range (particle size range) of these instruments is typically 1.25 to 250  $\mu$ . Grain-size measurements are made because contaminants generally are associated with the fine-grained particles [22]. This information can be useful in helping to delineate contaminated areas. Furthermore, grain size can be used to normalize other measurements and, at times, to predict when bioassays may encounter confounding factors.

## **IR Moisture Analyzer for Moisture Content**

Moisture content measurements can be made quickly in the field or laboratory using commercial IR drying instruments. Measurements are typically made by spreading a 5-gram sample of wet sediment on an aluminum sample dish, placing it in the analyzer, weighing it, initializing the drying procedure, and then re-weighing it. Percent moisture is determined by the difference between wet weight and dry weight. Drying time is typically 5 to 15 min, depending on moisture content. These results are used for conversion of data from wet weight to dry weight, for comparison with benchmarks and reference values, which are generally resolved in dry weight units. In some cases, percent moisture can be used as a proxy for grain size [1].

## **BIOLOGICAL TOOLS**

### **QwikLite™ Bioassay for Toxicity**

The QwikLite bioassay measures the inhibition of light emitted by marine bioluminescent dinoflagellates (e.g., *Gonyaulax polyedra*) exposed to a test solution (effluents, elutriates, or sediment pore waters). Any decrease in light output relative to controls suggests bioavailable contaminants or other stressors. The bioassays can measure a response within 24 hours of test setup and can be conducted for a standard 4-day acute test or 7-day chronic test. The bioassays can evaluate both acute and sublethal chronic effects from exposure to various toxicants. The dinoflagellates in the bioassay are at least as sensitive to organic and inorganic toxicants as mysid shrimp, silverside fish, chain diatoms, and sea urchins. The data from the bioassay can be correlated with more conventional toxicity tests, such as amphipod and sea urchin development [17], [23]. The QwikLite Testing System™ can be used for several different applications, including landfill leachate assessment, water treatment monitoring, effluent assessment, and sediment toxicity evaluation. If the contaminated sediment is toxic and requires cleanup, this technique can be used to assess the toxicity reduction [24]. A “Standard Guide for Conducting Toxicity Tests with Bioluminescent Dinoflagellates” is in the 1999 Annual Book of ASTM Standards [25].

### **P450RGS Dioxin Screening Assay for Sediment**

Numerous genotoxicity indicator and biomarker assays have been developed over the years for various purposes. In support of the Long-term Effects of Dredging Program (LEDO), existing assays were either modified or new assays were developed to more rapidly and cost-effectively detect contaminants, such as dioxins, PCBs, and PAHs that can cause genotoxic effects in dredged material intended for open-water disposal.

One such assay is the P450RGS biomarker assay. This assay uses a reporter gene system (RGS) based on cytochrome P450 to screen samples for a range of organic compounds, including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), coplanar polychlorinated biphenyl congeners, and high molecular weight polycyclic aromatic hydrocarbons. This screening method, Method 4255, will detect the total amount of planar compounds in solvent extracts of environmental samples of soil, sediment, tissue, and water [26].

The screening method was modified [27] so the assay could screen sediment extracts from dredged sediments for dioxin equivalences (TCDD EQs). The modifications have increased sample throughput and reduced the assay cost. This assay is reported to be less than one-tenth the cost of dioxin analysis using GC/MS and has comparable sensitivity [28].

## **cDNA Microarrays for Identification of Environmental Contaminants**

Emerging technologies for assessing the impact of environmental stressors on the aquatic environment are under development. One example is genomic screening tools such as DNA microarrays for the identification of unique patterns of genes that are “turned on” or “turned off” by specific environmental stressors [29]. This technology will ultimately provide a better understanding of processes from exposure to effect and reduce the uncertainty in assessing the risk of stressors in the environment.

Research by Inouye, Ang, and McFarland (2004) [30] shows the potential for using a cDNA array as a screening tool that identifies contaminants in environmental media (i.e., sediments) and toxic modes of action (MOAs) from contaminant mixture in sediments. MOA information can identify the type of time-consuming and expensive chronic sublethal bioassays (e.g., survival, growth, reproduction, genotoxicity) and costly and expensive chemical analysis that are needed, or demonstrate that these tools can be eliminated. A priori interpretations of the presence of known chemicals in sediment/soil samples are more defensible if accompanied by mechanistic information, i.e., MOA, and the resulting decisions are more certain.

While this type of assay does not fit the definition of rapid sediment characterization tools, it does offer potential for helping to understand the effects of contaminants on the environment, which is the most difficult, yet critical, part of understanding and managing environmental risk.

## **RSC TOOLS: HOW ARE THEY USED?**

Since the publication of the original RSC paper [1], RSC tools have been used to support multiple ecological risk assessments, as well as contaminated site restoration activities, TMDL assessments, and contaminant forensics used to identify sources of contamination during site assessments (Table 4). Scientists from the SPAWAR Systems Center San Diego (SSC San Diego) Environmental Sciences Branch performed the RSC analyses for each example listed in Table 4 and also provided data analysis and interpretation support. Other application of these tools can be found in published reports, many of which are accessible on the Internet (see Additional Resources section). Three examples from Table 4 (bold highlight) are summarized below to illustrate how RSC tools were used to support different Navy and non-Navy projects. References are provided to the complete reports from which information was drawn.

### **REMEDIAL INVESTIGATION/FEASIBILITY STUDY (RI/FS): HUNTERS POINT SHIPYARD, CALIFORNIA**

Hunters Point Shipyard (HPS), a formal naval shipyard located in San Francisco, California, was listed as a National Priorities List (NPL) site in 1989 and subsequently closed under Base Realignment and Closure (BRAC) in 1991. HPS is 866 acres in size, with one offshore parcel of sediment (Parcel F) comprising approximately 446 acres. Parcel F includes three marine habitats that blend with one another in transition zones: open-water aquatic, intertidal wetland, and bay mudflats. Many species of mobile marine animals (invertebrates, birds, and mammals) move among these habitats, either daily with the tides or seasonally.

Since 1991, various investigations have been conducted at Parcel F to evaluate shoreline and offshore contamination. The contaminants of concern identified in the surface and subsurface sediments include Hg, Cu, and PCBs.<sup>1</sup>

Between 1991 and 1998, two ERAs and one FS were carried out in Parcel F. Five areas were delineated as part of the area of concern referred to as the “low-volume footprint,” which represented the areas of highest ecological hazard. In the path towards finalizing the FS, which resulted in the development of remedial alternatives for the site, several additional studies were carried out that used the RSC tools.

### **Screening Survey in Support of HPS Validation Study (2000)**

The primary objective of the validation study was to more clearly define the extent of sediments that posed an unacceptable risk to the environment and that required evaluation in a FS of remedial options. The objectives of the screening survey were to (1) provide data density to support surface sediment contaminant concentration mapping, (2) provide supporting data for the validation study sample design, and (3) confirm the conceptual model for site chemistry. Surface sediment samples were collected in a grid pattern from 95 locations in the 5 areas that defined the low-volume footprint. The sediment samples were screened for lead (Pb), copper (Cu), zinc (Zn), and chromium (Cr) using XRF, and for PCBs using an immunoassay technique at the SSC San Diego laboratory in San Diego, California. Screening sample results were used to refine the sample design for the more detailed study of sediment chemistry, toxicity, and bioaccumulation.<sup>2</sup> In particular, the screening results were used to ensure that the validation study sample stations spanned the entire range of contaminant concentration and therefore represented the full range of potential exposure.

To fully utilize the RSC screening survey results and enable combination with other historical data, the RSC data were adjusted based on least squares regressions established between RSC data and fixed laboratory data from previous studies in the region as well as from data collected during the screening survey.<sup>2, 3</sup> Results from the regression analyses are shown for Cu and PCBs in Figure 1. After adjusting the screening results according to the regression equations and censoring PCBs at the limits of detection for the immunoassay (150 ppb), screening data were combined with other historical data for the same suite of constituents and plotted to evaluate the spatial distribution of contaminants in each area (Figure 2). By augmenting the historical data with the new screening results, excellent coverage of each area of interest was obtained, and these data were used to support the final validation study design for additional data collection at Hunters Point Shipyard.<sup>4</sup>

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<sup>1</sup> Barajas and Associates with Tetra Tech. 2007. “Revised Draft Feasibility Study Report for Parcel F Hunters Point Shipyard San Francisco, California.” Prepared for the Department of the Navy under Naval Facilities Engineering Command Contract Number N68711-03-D-5106, Contract Task Order 004 (May).

<sup>2</sup> Battelle, ENTRIX Inc., and Neptune and Co. 2000. “Hunters Point Shipyard Sediment Screening to Support Validation Study, Appendix C, Integrated Design for HPS Validation Stud,” Prepared for U.S. Navy, Naval Facilities Engineering Facilities Command, Southwest Division. March.

<sup>3</sup> Battelle, ENTRIX Inc., and Neptune and Co. 2000. “Hunters Point Shipyard Sediment Screening to Support Validation Study, Appendix B, Position Papers to Support HPS Validation Study.” Prepared for U.S. Navy, Naval Facilities Engineering Command, Southwest Division.

<sup>4</sup> Battelle, Entrix, Inc., and Neptune & Company. 2000. “Hunters Point Shipyard Parcel F Validation Study Work Plan.” September.

Table 4. Different applications of RSC tools (2001–2006).

Location	Year	RSC Tools/COC	Purpose
Ashtabula River, OH	2006	IA (PCBs)	Evaluation of environmental dredging for remediation of contaminated sediments.
Eagle Harbor, WA	2006	IA (PAHs)	Long-term monitoring of remedial capping effort.
NAF El Centro, CA	2006	FPXRF (metals), IA (PAHs)	Identify potential IR sites, pre-RI stage of RI/FS.
NAB San Diego, CA	2005	FPXRF (metals), IA (PAHs, PCBs)	Identify potential sediment contamination, pre-RI stage of RI/FS.
Quantico Marine Base, VA	2005	FPXRF (Pb), IA (DDT)	Identify potential sediment contamination, pre-RI stage of RI/FS process.
Sinclair and Dyes Inlet (Puget Sound Naval Shipyard), WA	2005	IA (PCBs)	Support ENVVEST TMDL study.
Skaggs Island Naval Facility, CA	2004	FPXRF (Pb), IA (DDT)	Support remedial monitoring during a removal action at a former dumpsite (guide step-outs during each phase of removal and compositing scheme).
<b>Duwamish River, WA</b>	2004	IA (PCBs)	Guide dredge area delineation. (TRIAD).
NAVSTA San Diego - Paleta Cr IR Sites 3&4, CA	2004	EDXRF (metals), IA (PAHs, PCBs, DDTs)	Identify potential sediment contamination, pre-RI stage of RI/FS.
Allen Harbor, RI	2004	EDXRF (metals), IA (PAHs)	Fingerprint PAH sources as part of FS (RSC used as initial screening of samples).
New London Sub Base, CT	2003	EDXRF (metals), IA (PAHs, PCBs)	Identify potential sediment contamination, pre-RI stage of RI/FS.
Elizabeth River Watershed, VA	2003	IA (PAHs)	Initial screen for fingerprinting projects.
<b>Sinclair and Dyes Inlet (Puget Sound Naval Shipyard), WA</b>	2002	EDXRF (metals)	Support ENVVEST TMDL study.
<b>Hunters Pt. Naval Shipyard, CA</b>	2000–2003	EDXRF (metals), IA (PCBs)	Support the RI/FS process.

IA: Immunoassay; FPXRF: Field-Portable XRF; EDXRF: Bench-top Energy-Dispersive XRF

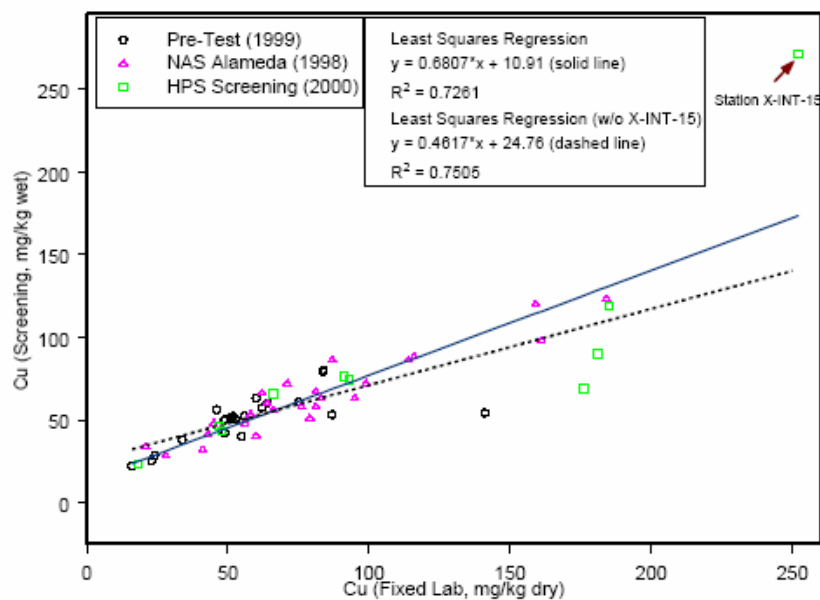
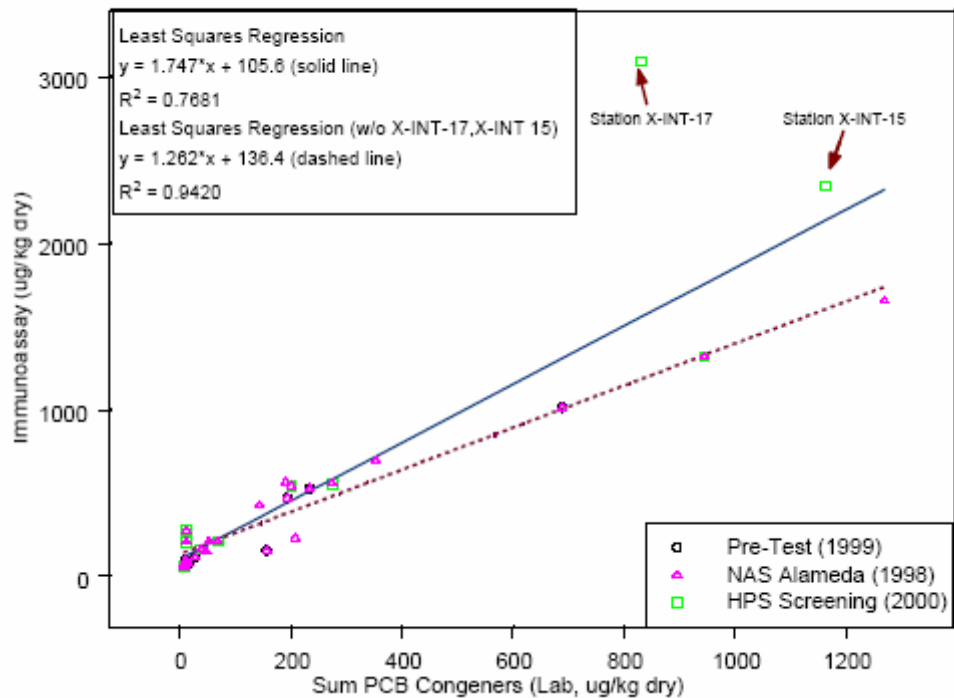


Figure 1. Hunters Point Shipyard, Parcel F offshore sediments. Correlation between historical lab data and screening data using least squares regression.<sup>5</sup>

<sup>5</sup> Ibid.

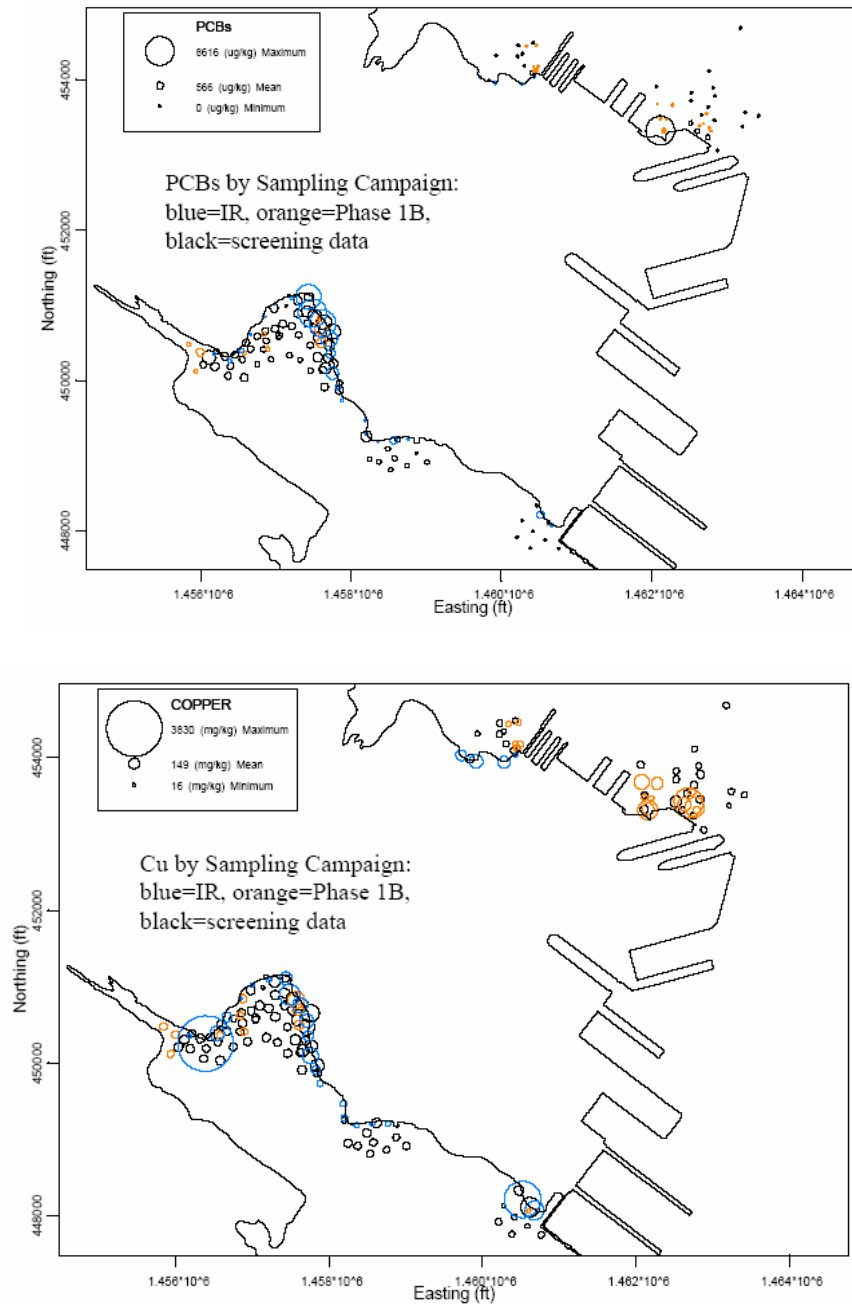


Figure 2. Hunters Point Shipyard, Parcel F offshore sediments. Bubble plots (mg/kg) for PCBs (top) and Cu (bottom) from historical and screening data combined.<sup>6</sup>

<sup>6</sup> Ibid.



### Feasibility Study Data Gaps Investigation (2003)

The primary goal of this investigation was to collect data to support the development and evaluation of remedial alternatives for offshore sediments in the South Basin and Point Avisadero areas (see Figure 2). The RSC tools were used in the South Basin to more clearly define the horizontal and vertical distribution of polychlorinated biphenyls (PCBs) in the sediment and possible onshore-to-offshore PCB transport pathways to ensure that all source areas were identified. Fifty-one cores were collected, subsampled, and analyzed for total PCBs, using an immunoassay method to provide detailed data on the horizontal and vertical distribution of PCBs. These data were used in conjunction with other historical data to infer the nature and location of PCB source areas in the South Basin. A subset of the samples were split and analyzed for PCB congeners by GC/MS to provide a comparative analysis between the rapid sediment characterization and GC/MS results as well as provide analyte-specific data.<sup>7</sup>

The horizontal and vertical distributions of total PCBs in the South Basin and along the adjacent shoreline were mapped using a combination of PCB screening (RSC) and laboratory (PCB congener) data to represent a snapshot of site conditions in 2003. The data set was used to generate a three-dimensional (3-D) model of PCB distribution. Plan view maps, representing horizontal slices at 0.5-ft intervals through the 3-D model, resulted in several observations for concentration of PCBs in surface and subsurface sediments. PCB concentrations in surface sediment were highest ( $>2,000$   $\mu\text{g/kg}$ ) at the north end of South Basin and decreased with increasing distance from the shoreline on the northeast side of South Basin. An area of higher surface concentrations ( $>250$   $\mu\text{g/kg}$ ) was apparent near the mouth of Yosemite Creek. Surface PCB concentrations over most of South Basin were  $<500$   $\mu\text{g/kg}$  (Figure 3, top). At a depth of 1 ft below the mudline, the area with PCB concentrations  $>2,000$   $\mu\text{g/kg}$  was more extensive, both at the north end of South Basin and at the mouth of Yosemite Creek. Overall, concentrations are higher 1 ft below the surface than at the surface (Figure 3, bottom). At 1.5 ft below the mudline, the area of highest PCB concentrations decreased in extent at the north end of South Basin, and increased in extent at the mouth of Yosemite Creek (Figure 4, top). At 2.5 ft below the mudline, PCB concentrations of  $>2,000$   $\mu\text{g/kg}$  at the north end of South Basin were limited to the vicinity of Station SB-076, whereas the affected area at the head of Yosemite Creek had not diminished substantially (Figure 4, bottom). The vertical limit of PCB concentrations  $>2,000$   $\mu\text{g/kg}$  at the head of Yosemite Creek was not delineated in this investigation based on an uncertainty analysis performed on the data as part of the DQO process.<sup>8</sup>

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<sup>7</sup> Barajas and Associates with Tetra Tech, op. cit.

<sup>8</sup> Battelle, SEA Engineering and Neptune and Company. 2005. "Draft Technical Memorandum Hunters Point Shipyard Parcel F Feasibility Study Gaps Investigation." Contract No. N68711-01-F-6102, 25 February, San Francisco, CA.

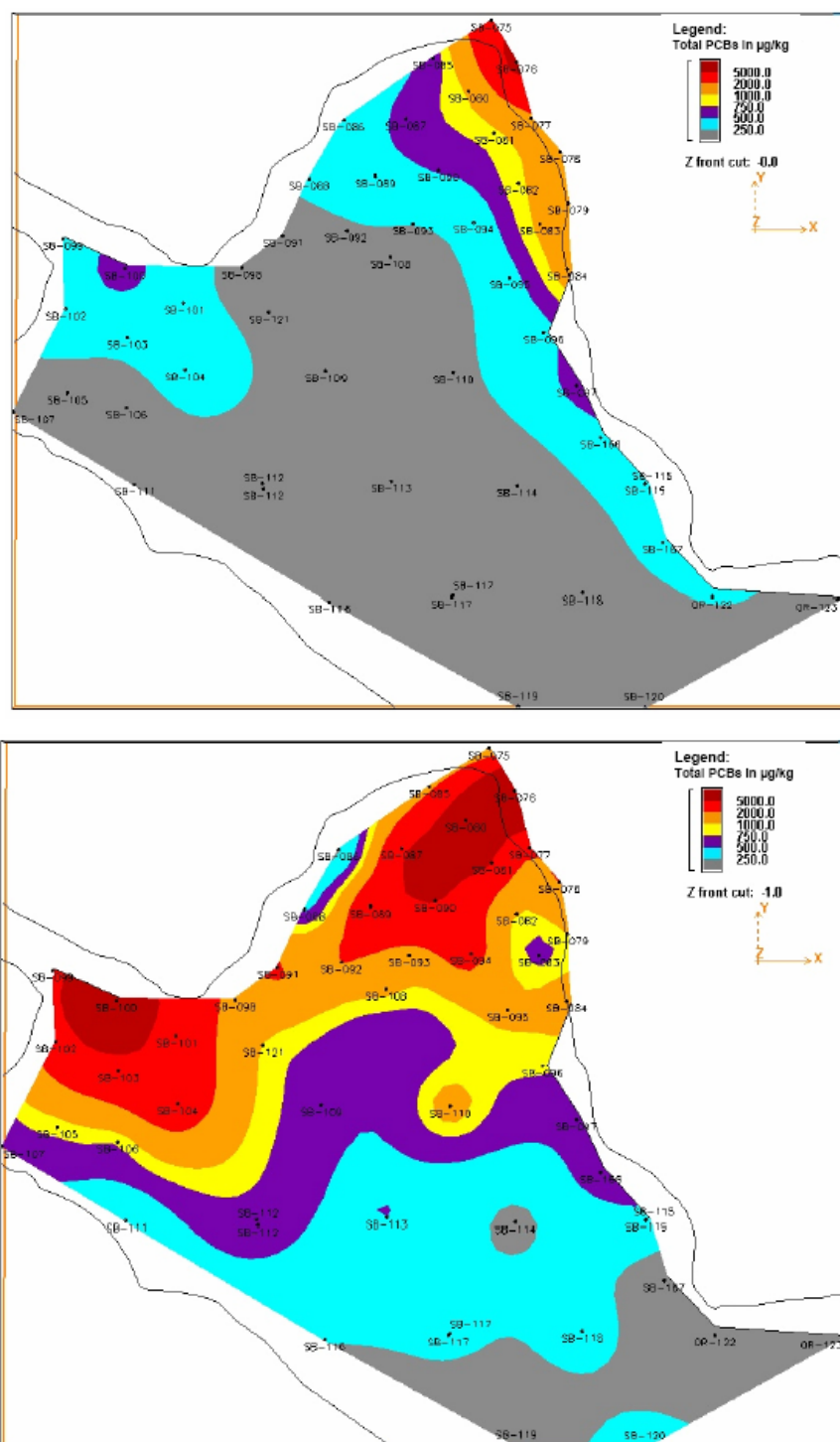


Figure 3. Hunters Point Shipyard Parcel F, South Basin. Plan view map representation of PCB sediment concentrations at 0.5 ft below mudline (top) and 1.0 ft below mudline (bottom).<sup>9</sup>

<sup>9</sup> Ibid.

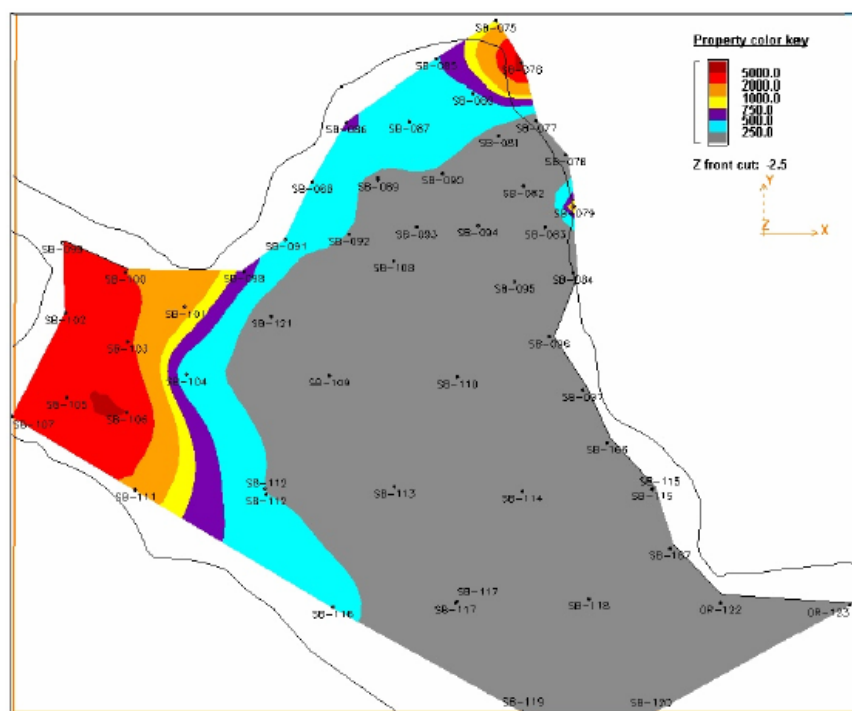
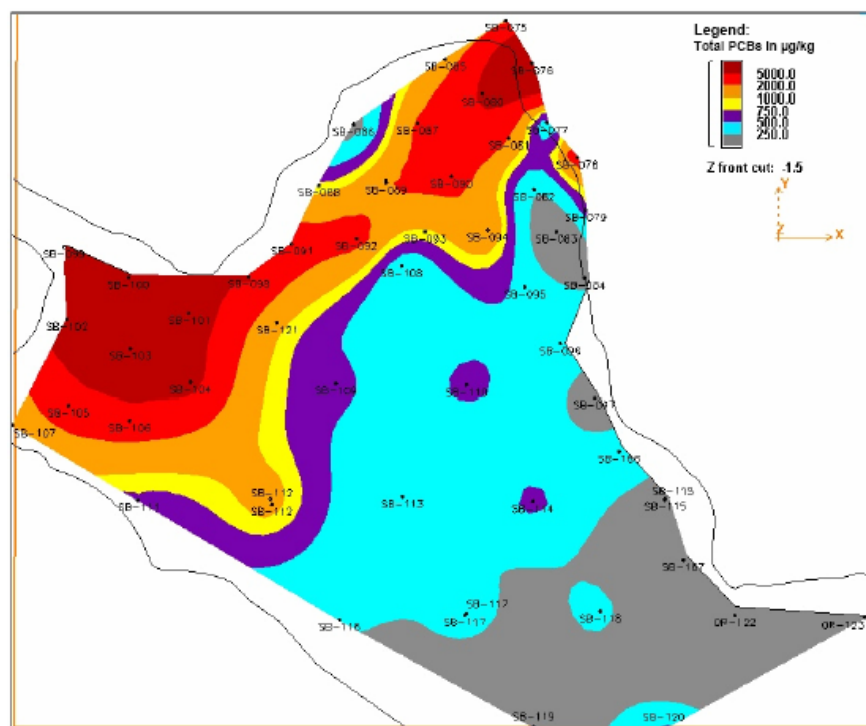


Figure 4. Hunters Point Shipyard Parcel F, South Basin. Plan view map representation of PCB sediment concentrations at 1.5 ft below mudline (top) and 2.5 ft below mudline (bottom).<sup>10</sup>

<sup>10</sup> Ibid.

The uncertainty analysis was carried out to ensure proper data analysis and interpretation of the RSC data. The detailed PCB distribution maps of South Basin are based largely on RSC data, although PCB congener data were used where available. The RSC data were correlated to confirmatory laboratory data for PCB congeners. The range of slopes for various regression models varied from 0.8 to 1.2, which suggested that the RSC results could be considered within 20% of the laboratory-derived value. PCB RSC data were adjusted by a factor of 1.1 for the analyses. A comparison between RSC and confirmatory laboratory results showed more scatter at high PCB concentrations; however, the primary range of interest for the Parcel F FS was 0 to 2000 µg/kg because concentrations above this range are above the proposed Preliminary Remediation Goals (PRGs). Therefore, accurate determination of PCB concentrations greater than 2000 µg/kg was considered less important than accurate determination of concentrations that were less than 2000 µg/kg.<sup>11</sup>

#### **TOTAL MAXIMUM DAILY LOAD (TMDL): SINCLAIR AND DYES INLET, WASHINGTON**

The Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF), the U.S. Environmental Protection Agency, the Washington State Department of Ecology, and other technical stakeholders are cooperating in an ENVironmental inVESTment (ENVVEST) project to develop and demonstrate alternative strategies for protecting and improving the ecological integrity of Sinclair and Dyes Inlets and their surrounding watershed in the Puget Sound, Washington.

Sinclair and Dyes Inlets, near Bremerton, Washington, are on the State of Washington 1998 303(d) list of impaired waters because of fecal coliform contamination in marine water, metals in sediment and fish tissue, and organics in sediment and fish tissue. Most of the data supporting the 303(d) listings were collected before 1999. Since that time, significant cleanup and source-control activities have been conducted in the inlets. A historical review concluded that existing data that were the basis of sediment listing may not be representative of current sediment conditions. In the case of target metals and organics, the recommendation was to establish whether present sediment metals concentrations supported the TMDL listings before proceeding with the TMDL study plan [31]. The RSC tools were used in support of two verification studies carried out for the target metals and organic compounds of interest. A summary of the metals verification study (MVS), which used the EDXRF, is provided below.

#### **Sediment Metals Verification Study (2003)**

The approach used for the MVS was to collect and analyze surface sediment samples from throughout Sinclair and Dyes Inlets and the adjoining water bodies (Port Orchard Passage and Rich Passage). A tiered analytical approach was used to facilitate the metals analysis for the large number of sediment samples collected for the study (n = 162).

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<sup>11</sup> Ibid.

The first step was to conduct XRF analysis of all 162 samples for a subset of target metals (Cu, Pb, Zn, Cd, and Ag), followed by analysis of a subset of the samples by ICP/MS for all target metals (Ag, As, Cd, Cr, Cu, Ni, Pb, and Zn). The criteria used for selection of the confirmation samples included selection of the following:

- Samples in which XRF result exceeded 90% of the Sediment Quality Standard (SQS) for one or more target metals (Cu, Pb, and Zn)
- At least three samples in 303(d) segments listed for Cd or Ag (because XRF screening does not detect these metals at levels comparable to state SQS),
- Samples in which XRF result was different (much higher or lower) than expected
- Additional samples to represent the range of concentrations observed for each target metal

To predict the actual metal concentrations from XRF data, quantitative analytical results for the 40 confirmatory samples were plotted against the XRF results for the same samples. Positive linear correlations were developed for Pb, Cu, and Zn, which were the only metals reliably detected by XRF in the most samples (Figure 5). Each metal had one outlier sample, probably because of sample heterogeneity, as the outlier samples were all located in between piers where variable particulate metal concentrations are expected. When these outlier values were removed from the correlation, the XRF results for Cu and Pb correlated very well with ICP/MS results ( $R^2$  values were 0.876 for Cu, 0.932 for Pb). Zn measured by XRF correlated well with ICP/MS results ( $R^2$  of 0.730), especially up to XRF concentrations of 200 ppm. However, when the XRF concentration for Zn was 250 ppm or higher, there was much more variability between data points, and the linear relationship between the two methods did not appear to be as strong. The resulting linear equations with outliers removed were used to predict a definitive metal concentration from the XRF result for those samples that did not receive confirmatory analysis.

The MVS results show that sediment quality in Sinclair Inlet has improved markedly since implementation of cleanup and source control actions, and that the distribution of residual contaminants is limited to near-shore areas already within the actively managed PSNS Superfund site where further source control actions and monitoring are underway. Outside the immediate vicinity of the PSNS Superfund site in Sinclair Inlet, the target metals concentrations met state SQS [36].

### **TRIAD: LOWER DUWAMISH RIVER, WASHINGTON**

This field investigation was conducted to define patterns and determine source(s) of PCBs in a reach of the Lower Duwamish River, Seattle, Washington, and to generate data to guide RI/FS and corrective measures study decisions. The full report, “Use of PCB Immunoassay to Investigate a Contaminated River Reach in the Lower Duwamish Waterway, Seattle, Washington,” is available online at <http://www.triadcentral.org/user/index.cfm>.

The TRIAD approach (systematic project planning, a real-time measurement system, and a dynamic work strategy) was implemented to assist the USEPA in resolving a two-year dispute between two potential responsible parties over the responsibility of PCB contamination at a river reach of the Lower Duwamish River. The U.S. Army Corp of Engineers proposed to use the Triad approach during Technical Project Planning meetings with USEPA, and received additional support from USEPA’s Office of Superfund Remediation & Technology Innovation, Technology Integration & Information Branch to test the application of the immunoassay technology.

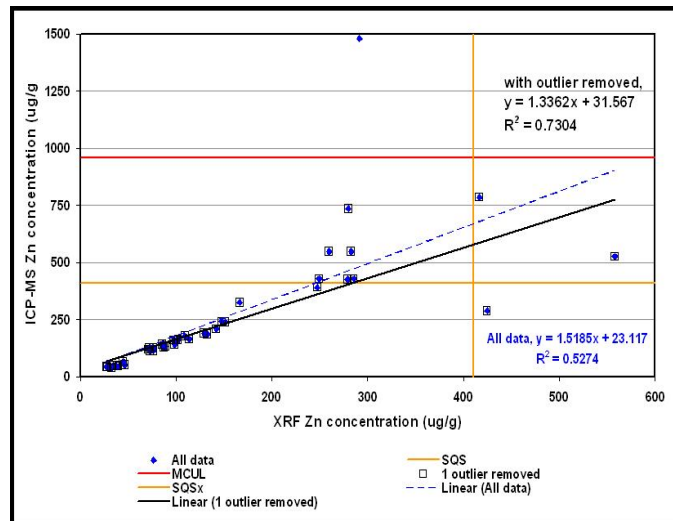
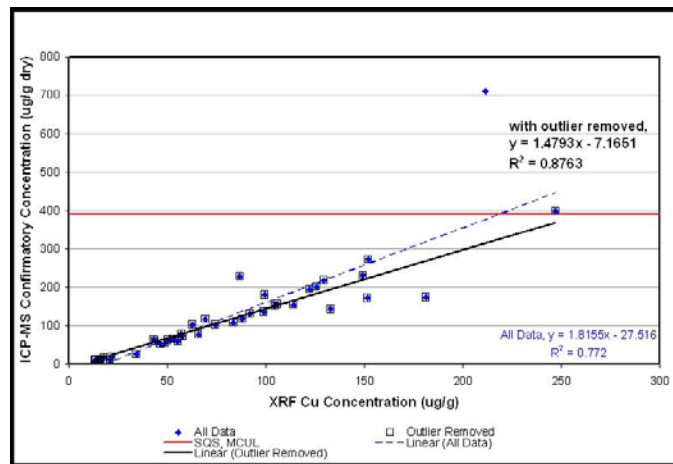
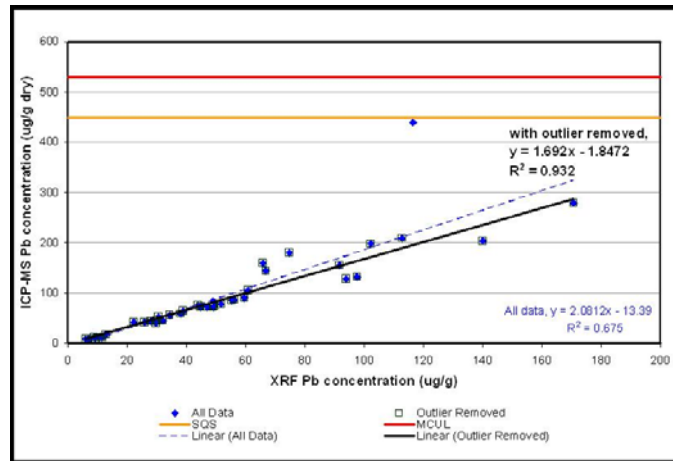


Figure 5. Linear correlations of XRF and ICP/MS measurements for Cu (top), Pb (middle), Zn (bottom), ENVVEST MVS [31].

The project objectives were to (1) characterize the upstream origin and extent of contamination by PCBs to the Lower Duwamish Waterway from a known downstream contamination pattern to further evaluate risks posed to humans and aquatic organisms; and (2) determine boundaries between adjacent riverside property-owners' contributions to the PCB plume. Additionally, specific data collection objectives were developed in support of the project and to demonstrate the utility of field methods (Demonstration of Method Applicability [DMA]). The objectives included (1) a determination of decision error rates for the immunoassay kits, (2) a comparison of samples against regulatory criteria using both methods, and (3) a comparison of the size of sediment removal (dredge depth) required as indicated by the two methods.

A total of 97 samples were collected, split, and analyzed by the immunoassay kits and the laboratory. Of those samples, 17 were misclassified by the immunoassay kits based on false negative errors and 6 samples were misclassified based on a false positive error relating to the lower and higher risk-based standards established by the State of Washington. The differential sensitivities (cross-reactivities) of the immunoassay for the Aroclor<sup>®</sup> composition of the samples were also assessed. The immunoassay is calibrated for Aroclor<sup>®</sup> 1254, with published relative sensitivities of 117% to Aroclor<sup>®</sup> 1248 and 64% to Aroclor<sup>®</sup> 1260.

It was determined that the primary sources of error were related to (1) cross-reactivity, (2) within-sample heterogeneity, and (3) water content in the samples (greater amounts of water reduced the efficacy of the methanol extract). The latter two sources of error can be minimized in the field by thorough sample mixing and decanting excess water before extraction. However, addressing the issue of sensitivity is more challenging and can require additional post-sampling interpretation frameworks. In this case, for example, the decision point for the low-risk-based standard was adjusted downward to determine if the false negative rate could be reduced without affecting the false positive error rate.

Ultimately, it was concluded that the immunoassay data were sufficient to address the concern that separate PCB releases associated with the bank along the property of one of the named PRPs had occurred and had led to subsurface contamination. However, the test somewhat underestimated the absolute extent of the surface contamination.

Triad had two principal benefits for this investigation. First, immunoassays were used in conjunction with data visualization to place new samples at locations of greatest utility in defining hot-spots and determining depth-wise patterns in sediment cores. Second, the retrospective data analysis showed the utility of the immunoassay kits in overall uncertainty management. Because of the large collaborative (immunoassay and laboratory) data set, it was possible to look at the overall decision uncertainty with and without immunoassay screening [32].

## **RSC TOOLS: COST COMPARISON**

Table 5 provides an example of integrating rapid sediment characterization tools into the assessment process. In this example, to delineate the horizontal and vertical extent of contamination for metals and PCBs, 300 sampling positions were identified. By measuring samples from each station using two RSC tools (XRF and immunoassay), and then down-selecting 60 samples for standard laboratory analysis, the overall analytical cost could be reduced by a little more than 50% as compared to the cost of analyzing all of the samples using standard analytical methods. The cost could also be reduced by taking fewer samples

for standard laboratory analyses; however adequate coverage/delineation of the site would be compromised. By using RSC tools with lab validation, better delineation of a site could be accomplished in a cost- and time-effective manner.

The amount of money saved in analytical costs is only one benefit of using RSC tools as part of a project. Improved investigation quality arises from better focus on project goals, increased sample coverage of the site, fewer unexplored site uncertainties, flexibility for field activities to adjust to unexpected conditions, and sophisticated data management tools to analyze and communicate the findings.

Table 5. Cost benefit comparison for 300 samples.

Analysis Method	RSC Tool [1] (# of Samples)	Standard Method [2] (# of Samples)	Total Cost (\$)
XRF [1] (metals) (\$75/sample) (40 samples per day)	n = 300	n = 60	29,700
ICP/MS [2] (metals) (\$120/sample) (30- to 90-day turnaround)	n = 0	n = 300	36,000
Immunoassay [1] (PCBs) (\$100/sample) (20 to 30 samples per day)	n = 300	n = 60	60,000
GC/MS [2] (PCB congeners) (\$500/sample) (30- to 90-day turnaround)	n = 0	n = 300	150,000
Total cost (RSC + lab validation)			89,700
Total cost (laboratory only)			186,000

As discussed in the examples presented in the previous section, the overall efficiency (e.g., lower cost, less sampling/analysis iterations) of each project was improved by using RSC tools. The ability to provide higher data density at lower costs supported additional regulatory sampling designs at Hunters Point Shipyard, provided sediment concentration mapping for Sinclair and Dyes Inlet TMDL studies, and supported the development of conceptual site models for site chemistry in the Duwamish River.

## RSC TOOLS: RECOMMENDATIONS FOR USE

During the time in which this report was originally published, RSC tools were just beginning to be incorporated into site assessments. Because of the uncertainty associated with their use, several recommendations were offered to support potential users of these technologies. Since that time, field analytic tools have been used to support a myriad of different field activities. Furthermore, a great deal of information, such as guidance documents and standard methods, case studies, and information on developing technologies, is readily available to the public.



A review of the current literature not only supports the principles originally presented, but also greatly expands on them and provides many more factors critical to the successful implementation of field analytic tools. While a discussion of all of these factors is beyond the scope of this report, a review of the original recommendations, with links to an expanded discussion of each recommendation, is provided.

## **DETERMINE WHICH TOOLS ARE APPROPRIATE**

To determine if RSC tools are appropriate to define the nature and extent of contamination at a given site, site-specific project goals and parameters as defined by the Data Quality Objective (DQO) process must be considered. It is critical to ensure that the contaminants or criteria that are decision drivers be detectable with the RSC tools that are available. In most cases, even if screening tools are not available for all the contaminants of concern, the tendency for classes of contaminants to co-associate allows one to use those parameters that are more easily measured to act as proxies for a suite of contaminants, to guide sampling, and to interpolate between samples where a full suite of analyses is undertaken. In all cases, RSC technologies should be supplemented with a subset of samples for which thorough, traditional, standard laboratory analyses are carried out (see Technology Selection at <http://www.triadcentral.org/mgmt/meas/select/index.cfm>).

## **DATA QUALITY**

As with any method or technology, certain limitations exist. The primary limitations to RSC technologies are that they are often (1) non-specific, (2) semi-quantitative, and (3) matrix-sensitive. Because of these limitations, the data produced by RSC tools/methods are not necessarily equivalent to those generated by standard methods. Data are typically classified as “screening data with definitive confirmation” or “definitive data” [17]. Screening data are data generated by rapid, less precise methods of analysis with less rigorous sample preparation, such as those produced using RSC methods, whereas definitive data are generated using rigorous analytical methods, such as the approved EPA reference methods. Definitive data are analyte-specific, with confirmation of analyte identity and concentration [17]. Depending on the data quality requirements established during the DQO process, a well-designed RSC protocol paired with laboratory validation will provide a collaborative dataset that can be of sufficient quality and great value to the field activity (see QA/QC Concepts at <http://www.triadcentral.org/mgmt/qa/concepts/index.cfm>).

## **DOCUMENTATION AND REPORTING OF DATA**

Documentation and reporting is a very controversial subject in environmental analytical chemistry because it affects how data are received and perceived by the user and often the public [18]. The advent of database and GIS tools for the presentation and processing of environmental data allows for an unprecedented level of data manipulation and interpretation not just by data generators, but also other users, regulators, and stakeholders. While this ability has many benefits, potential dangers exist as well, particularly when data from many sources are combined. Results can be misleading if non-equivalent data are combined together without careful intercalibration. A few different approaches to the documentation and reporting of data can be used to avoid such problems when reporting results, particularly those from RSC methods. The first is to always flag numbers generated by a non-standard method in spreadsheets and data reports, and to include text, references, or qualifiers that address any potential offsets from standard analyses. This method has the advantage that all data are available to regulators and stakeholders, but information necessary for proper interpretation is

also provided. A second approach is to perform site-specific calibration of RSC analyses and to report only corrected, calibrated data. This method has the advantage of providing results that are more easily interpolated between or contoured with standard data. However, site-specific calibration requires a higher level of effort at a site (possibly more samples sent for laboratory analyses) and may reduce the cost-effectiveness and utility of using RSC tools. A third option, particularly for RSC analyses that generate only qualitative data (i.e., data that identify the presence or absence of target analytes, but may have no relationship to true analyte concentrations) is to not report values. In such an approach, samples are ranked (e.g., from highest to lowest levels) or ranges are reported (e.g., below detection limit, detected but unquantifiable, below action limit, above reference levels, etc.). (See Information Management at <http://www.triadcentral.org/mgmt/log/infomgmt/index.cfm>.)

## **OBTAIN REGULATORY ACCEPTANCE BEFORE USE**

A concern voiced by many potential users of RSC tools is that field data will not stand up to regulatory or legal scrutiny. While these concerns are not trivial, it is clear that there are a growing number of case studies in which RPMs, regulators, and the user community have accepted RSC data as a critical, though not stand-alone, part of the analytical and decision-making process. Clearly, the rules on the legal defensibility of scientific data do not distinguish between measurements made in the field and measurements made in the laboratory. The rules used by the courts are very different than those established in regulation. In particular, courts have found that evidence may be reliable even if there were major deviations from methods specified in regulation, or if the analysis was done in a non-accredited laboratory, even if accreditation were required by regulation. As to the weight that is put to evidence, the validation of the method and the quality system documentation are certainly relevant [4].

The intent to use RSC tools, and how the resulting data will be interpreted and managed, should be addressed up front with regulators and other stakeholders. Furthermore, RSC tools are only one part of the process, which should always be balanced with and supplemented by standard, certified analyses. When used appropriately, RSC tools can streamline many aspects of various field activities, delineating areas of concern, filling in information gaps, and ensuring that expensive, certified analyses have the highest possible impact (see Real-Time Data and Regulatory Participation at <http://www.triadcentral.org/reg/realtime/index.cfm>).

## **OTHER FACTORS FOR CONSIDERATION**

The Triad Resource Center (<http://www.triadcentral.org/index.cfm>) provides perhaps the most comprehensive overview of key concepts critical to the application of field analytic tools. While the Triad approach is not a new environmental program, it does bring together concepts articulated in a variety of other initiatives and programs into a single integrated package. While the intent of the TRIAD approach is to support decision-making for hazardous waste site characterization and remediation, the principles discussed within its framework are relevant to the appropriate application of RSC tools, regardless of the program for which they are used (e.g., TMDL studies, forensic studies, etc.). While the factors discussed above are important to the successful selection and implementation of field analytical tools, there are other factors such as understanding site-specific conditions, sampling design, budget, etc. that must be considered.

When the interplay of these factors is understood, screening methods can play important roles in generating data that are effective for making defensible project decisions while simultaneously improving the cost-effectiveness and efficiency of site restoration activities.

## ADDITIONAL RESOURCES

The information provided in Table 6 represents the most current resources on innovative technologies, including field analytical tools. The location of items may change as menus and homepages are reorganized.

Table 6. Additional resources for innovative technologies.

Host	Description	Internet Address
U.S. Environmental Protection Agency (USEPA)	Clu-In Hazardous Waste Cleanup Information: Characterization and Monitoring, Tools Description and Selection	<a href="http://www.clu-in.org/char1_tech.cfm#tech_sele">http://www.clu-in.org/char1_tech.cfm#tech_sele</a>
	Dynamic Field Activities	<a href="http://www.epa.gov/superfund/programs/dfa/index.htm">http://www.epa.gov/superfund/programs/dfa/index.htm</a>
	Measurement and Monitoring Technologies for the 21st Century: Technology Focus Areas	<a href="http://clu-in.org/programs/21m2/focus/">http://clu-in.org/programs/21m2/focus/</a>
	SW-846 Methods On-Line	<a href="http://www.epa.gov/SW-846/main.htm">http://www.epa.gov/SW-846/main.htm</a>
	Superfund Technology Innovative Evaluation Program	<a href="http://www.epa.gov/ORD/SITE/">http://www.epa.gov/ORD/SITE/</a>
Triad Resource Center	Innovative approach to decision-making for hazardous waste site characterization and remediation.	<a href="http://www.triadcentral.org/">http://www.triadcentral.org/</a>
Interstate Technology and Regulatory Council (ITRC)	State-led national coalition dedicated to better environmental protection through innovative technologies.	<a href="http://www.itrcweb.org/">http://www.itrcweb.org/</a>
Federal Remediation Technologies Roundtable (FRTR)	Federal Government Interagency Effort to provide technical information on technologies for waste site cleanup.	<a href="http://www.frtr.gov/">http://www.frtr.gov/</a>
U.S. Department of Defense Environmental Security Technology Certification Program (ESTCP)	Promotes innovative, cost-effective environmental technologies through demonstration and validation at DoD sites.	<a href="http://www.estcp.org/">http://www.estcp.org/</a>
U.S. Navy	SSC San Diego Environmental Sciences Branch	<a href="http://environ.spawar.navy.mil/">http://environ.spawar.navy.mil/</a>
	NAVFAC Environmental Restoration Technology Transfer (ERT2)	<a href="http://www.ert2.org/ert2portal/DesktopDefault.aspx">http://www.ert2.org/ert2portal/DesktopDefault.aspx</a>
U.S. Army Corps of Engineers (US ACoE)	Engineer and Research Development Center: Environmental Laboratory	<a href="http://el.erdcl.usace.army.mil/index.cfm">http://el.erdcl.usace.army.mil/index.cfm</a>
U.S. Air Force	Air Force Center for Engineering & the Environment	<a href="http://www.afcee.brooks.af.mil/">http://www.afcee.brooks.af.mil/</a>



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<b>4. TITLE AND SUBTITLE</b>  RAPID SEDIMENT CHARACTERIZATION TOOLS				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHORS</b>  V. J. Kirtay				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> SSC San Diego San Diego, CA 92152-5001				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  TR 1970	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Office of the Chief of Naval Operations Naval Facilities Engineering Command Director, Environmental Readiness (N45) 1322 Patterson Avenue, Suite 1000 Washington, DC 20374-5065				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
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<b>15. SUBJECT TERMS</b> Mission Area: Environmental Science rapid sediment characterization      total maximum daily load      ultraviolet fluorescence spectroscopy site assessment      x-ray fluorescence spectrometry      immunoassays					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			V. J. Kirtay
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